Project Report: Delivery of Organic Materials to Planets

Arizona State University
Executive Summary
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Astrobiologists and their multidisciplinarian colleagues are writing a preliminary outline of the story of life on Earth and in space. They are studying the processes that led to an environment capable of supporting life on Earth, the basic building blocks of life, the origin and evolution of Earth's living systems, and they are exploring other places in our Solar System, such as Mars and Europa, for evidence of life.

Overview of Astrobiology at Arizona State

Astrobiology is the emerging interdisciplinary science that studies the origin, evolution, distribution, and future of life in the cosmos. Arizona State University supports a broadly based program of research and training in astrobiology that addresses the first three of these areas. The following paragraphs provide an overview of the specific research currently being addressed by the Arizona State University (ASU) Astrobiology team, along with selected highlights of research progress during Year 4. With such a large and diverse team, it is simply not possible to cover all details of the research progress made over the past year in the space provided. For a more complete review, the reader is referred to the individual detailed ASU project reports.

Origins of the Basic Building Blocks of Life

At ASU, the origin of living systems is being approached through (1) studies of the cosmoschemistry of carbonaceous meteorites and (2) studies of abiotic synthesis of organics in deep−sea hydrothermal vent environments. In support of this work, ASU maintains a jointly funded (NASA−NSF−ASU) Ion Microprobe Facility, a state−funded Center for Meteorite Studies (which harbors the largest university−owned meteorite collection in the world) and an NAI−funded Hydrothermal Systems Laboratory, capable of simulating pressure, temperature, and chemical conditions of deep seafloor black−smoker vent systems.

<u>Meteorite Cosmochemistry</u>: A research group is studying the chemistry of carbonaceous meteorites. Among the oldest objects in the Solar System, these objects provide insight into the exogenous (extraterrestrial) origins of the organic building blocks that make up living systems. This group also studies the isotopic composition of Martian meteorites as a basis for assessing the nature of the carbon reservoir on Mars.

During Year 4, the meteorite studies group published an initial analysis of the Tagish Lake meteorite, a carbonaceous chondrite that fell on a frozen lake in Canada in January of 2000. Because of the unique circumstances of the fall, the Tagish Lake meteorite is thought to be the most pristine carbonaceous meteorite discovered to date, thus providing an unprecedented opportunity to analyze samples that are essentially free of terrestrial contamination. Through the efforts of the Center for Meteorite Studies, ASU was able to acquire half of the 10−gram sample made available for study by the owner. The study, published in *Science* (Pizzarello et al (2001)), characterized both the soluble organic suite and the insoluble macromolecular carbon fraction of the meteorite, establishing its unusual composition in relation to previously studied carbonaceous meteorites.

Research into the nature of hydrous alteration environments on carbonaceous meteorite parent bodies was also completed and accepted for publication in *Geochemica et Cosmochemica Acta*. Using a combination of oxygen isotopic, electron microprobe, and petrographic methods, this study established the nature and timing of aqueous alteration processes on the meteorite parent body.

<u>Abiotic Synthesis of Organics in Hydrothermal Environments</u>: An effort is under way to understand the synthesis of pre−biotic organic compounds at high temperatures, specifically within seafloor black−smoker hydrothermal systems.

During Year 4, the hydrothermal group demonstrated experimentally that under seafloor hydrothermal conditions, hydrogen, carbon dioxide and water react in the presence of the mineral magnetite to form methanol, an important precursor organic molecule (Voglesonger et al (2001). *Chemical Geology*). In addition, building on kinetic studies of the conversion of smectite clay to illite, this group also began experiments designed to follow the conversion of methanol to more complex organic molecules in the presence of clays. Work over the past year demonstrated that smectite clay−methanol−ethanol systems at 1,000 bars pressure and 300°C, synthesize a rich variety of organic compounds and that the relative abundance of those compounds changes with reaction time over a 4−week period. Compounds identified so far include alkanes, branched phenyl compounds, bicyclic aromatics, and sterates.

In the fall of 2001, we participated in an NSF−supported field excursion to latitude 9°N on the East Pacific Rise, using the deep submersible *Alvin.* This field expedition afforded an opportunity to deploy *in situ* experiments to monitor the microbial colonization of young black−smoker chimneys and to collect a large “living” chimney for carrying out NAI−supported studies of microporosity. The porous internal structure of sulfide chimneys in seafloor systems may provide important sites for concentrating pre−biotic organic molecules. The microporous internal structure of the smoker has been characterized using synchrotron x−ray tomography and new computational methods developed to visualize porosity with a resolution of about 10 microns (Ashbridge et al (Submitted). *Computers and Geology*).

Early Biosphere Evolution

At ASU, the early evolutionary history of living systems on Earth is being addressed through (1) ecological and molecular studies aimed at understanding the origins of photosynthesis(2) studies of microbial fossilization in modern environments, with applications for interpreting biosignatures preserved in ancient rocks, (3) new approaches to interpreting paleoenvironmental conditions on the Archean Earth and early Mars, and (4) an improved understanding of the role of impacts in shaping biosphere evolution. Research in each of these focus areas is being applied to the development of strategies for the astrobiological exploration of Mars.

<u>Evolution of Photosynthesis</u>: The appearance of oxygenic photosynthesis is regarded as one of the most important evolutionary events in the development of our biosphere. The accumulation of photosynthetic oxygen in Earth's surface environments ultimately paved the way for the origin of advanced multicellular life forms and human intelligence.

A research group is studying the origin and evolution of photosynthetic systems through a broadly based interdisciplinary collaboration involving a half dozen partnering universities.

During Year 4, this team made progress in four primary areas: (1) whole genome comparative analyses of photosynthetic organisms, (2) the search for phototrophs in non−solar environments around hydrothermal vents, (3) field and laboratory studies of photosynthetic organisms in thermophilic and iron−rich environments, and (4) biochemical analyses of primitive phototrophic organisms. In addition, Co−I Blankenship published his book, *Molecular Mechanisms of Photosynthesis* (2002). Blackwell Science Oxford).

Whole genome sequences recently became available for representatives of all major groups of photosynthetic organisms. Analysis of these genomes using newly developed analytical methods for molecular phylogeny (Zhaxybayeva and Gogarten (2002). *EMC Genomics*) showed that large−scale horizontal gene transfers have taken place (Olendenski et al (2002). *Cellular Origin and Life in Extreme Environments*. Kluwar Pub.) and that the evolution of photosynthetic systems occurred as a complex mosaic process involving several gene transfers (Xiong and Bauer (2002). *Annual Reviews of Plant Biology*).

Over the past year, the same group continued to search for novel phototrophs by exploring the non−solar environments around hydrothermal vents. Deep−sea hydrothermal vents emit a small amount of fluorescent light from both thermal and nonthermal sources. This emitted light has been suggested as a potential energy source for photoautotrophic organisms. In December 2001, the team participated in a field expedition to explore hydrothermal vents of the Nine North vent system of the East Pacific Rise, using the deep submersible *Alvin*. Photosynthetic organisms were collected near the vents and are now in laboratory culture. Experimental controls were established to determine if these pigmented organisms are indigenous to the vent environment, or if they represent contamination from surface photic environments. Additional work to measure the light at vents was carried out at sites along the Mid−Atlantic Ridge and gave results similar to those obtained from vents in the Pacific (White et al (In Press). *Geophysical Research Letters*). This work on alternative energy sources has important implications for exploring for habitable environments elsewhere in the Solar System (e.g., deep ocean floor environments of Europa).

Field and laboratory studies of photosynthetic organisms in iron−rich environments have shown that some photosynthetic organisms can utilize reduced iron as an electron donor. This has important implications for understanding the origin of banded iron formations in the Precambrian and for interpreting the rise of atmospheric oxygen. Mutant proteins that are potential candidates for Fe−oxidizing complexes have now been isolated and analyzed.

To better understand the metabolism and reactive oxygen protection strategies of primitive photosynthetic organisms, detailed biochemical analyses were made of a number of proteins obtained from the deep branching thermophilic photosynthetic organism, *Chloroflexus aurantiacus*. Proteins studied included superoxide dismutase, auracyanin (a copper protein thought to be involved in photosynthetic electron transfer) and several multi−subunit cytochrome electron transfer complexes.

<u>Interpreting Biosignatures in Ancient Terrestrial and Extraterrestrial Materials:</u> Recent controversies over the biogenicity of the oldest terrestrial fossils, as well as the origin of putative fossil biosignatures in Martian meteorite ALH 84001, have highlighted the need to develop more robust chemical and morphological criteria for the recognition of ancient environments and fossil biosignatures in ancient rocks. At ASU, an interdisciplinary effort is under way to address important issues in fossil biosignature detection within ancient terrestrial and extraterrestrial materials and to discover new approaches to reconstructing ancient environmental conditions on the early Earth.

Studies are in progress to understand the processes of microbial fossilization and microbialite morphogenesis in modern extreme environments, including hydrothermal springs and hypersaline lake environments located in North America and Mexico. These studies are yielding information from modern analogs that can be used to interpret the ancient biogeologic record on Earth and potentially, Mars. (Farmer (2001). *Palaeobiology II*, Blackwell Science). During Year 4, studies of the microbial paleontology and morphogenesis of oncolitic stromatolites (spherical stromatolites formed by rolling) in riverine and lake environments of the Cuatro Cienegas Basin, Central Mexico were begun. Electron and light microscopy showed that oncoids possess distinctly zoned microbial communities consisting of a surficial assemblage of larger (>10−micron diameter) filamentous cyanobacteria and diatoms, overlying a subsurface community (1−2 mm depth) that is dominated by finely filamentous and coccoidal (<2 micron−diameter) bacteria. Collaborative molecular studies were undertaken to establish the taxonomic affinities of the above morphotaxa. Pervasive carbonate precipitation and lithification of oncoids appears to be controlled by the metabolic activities of the deeper community. Calcium electrode measurements with German collaborators, confirmed the rapid sequestering of calcium at the depth of the subsurface community. Within oncoid interiors, a well−preserved microbial fossil assemblage occurs as permineralized sheaths and filament molds, with assemblages being dominated by the finely filamentous component of the subsurface filamentous community.

Analytical transmission electron microscopy (ATEM) was used to characterize the nanometer−scale microstructure and composition of kerogenous microbial biosignatures preserved in the 2.0−Ga (billion years before the present) Gunflint Formation. Electron energy−loss spectroscopy (EELS) confirmed that microfossils are composed of amorphous kerogen concentrated along grain boundaries of microquartz. Kerogen is amorphous, showing little evidence for graphitization. In coccoidal microfossils, kerogen forms cell−wall−like features around cores of granular microquartz, whereas in filamentous forms, the kerogen is disseminated along needle−shaped grain boundaries that separate submicron−sized fibers of chalcedonic quartz. Similar methods are being applied to the study of putative biosignatures in the controversial 3.5−Ga Apex Chert from Western Australia. The goal is to characterize the composition, crystallinity, and distribution of the kerogen to determine if this material is biogenic or inorganic hydrothermal in origin.

New methods of electron tomography and holography were applied to evaluate the biogenicity of putative magnetite biosignatures in Martian meteorite ALH845001 (Buseck et al (2002). *Proceedings of the National Academy of Sciences*). The strongest argument for the biogenic origin of magnetite crystals in Martian meteorite ALH 84001 has been based on their proposed morphological and geochemical similarity to magnetite crystals produced by terrestrial magnetotactic bacteria. New techniques made it possible to determine the shapes of both ALH84001 and biogenic magnetites more accurately than was previously possible. Although the methods yielded significantly improved three−dimensional (3−D) shape reconstructions, it was concluded that the magnetite crystal shape is still not sufficiently well understood to permit us to distinguish between inorganic and biogenic forms. In addition to refining the techniques for shape analysis, an automated phase unwrapping algorithm for quickly processing tomographic holograms from TEM data was developed.

<u>Inferring Paleoenvironmental Conditions on Early Earth and Mars</u>: Extreme variations in oxygen isotopic abundances for modern, basalt−hosted caliche deposits (carbonate precipitates formed during the arid weathering of mafic volcanic rocks) have been documented. Values obtained from exposed caliche surfaces were enriched in ^{18}O, probably as a result of intense evaporation. However, at the same locations, subsurface caliche deposits exhibited relatively light carbon values, indicative of a biological source (Knauth et al (Submitted). *Geochemica et Cosmochemica Acta*). Because of the prevalence of basalts on Mars, these geochemical relationships have important implications for the exploration of that planet. Caliche would be expected to form under the warmer, wetter climate that has been frequently postulated for early Mars. Indeed, the discovery of caliche deposits within ancient Martian basalts would provide direct evidence for aqueous weathering processes, whereas light isotopic values in subsurface profiles may constitute a robust chemical signature for life. The model for hypersalinity of the Archean oceans was further refined and a paper published on the potential for eutectic brines in

the Martian subsurface as a mechanism for creating modern seep features observed at high latitudes (Knauth and Burt (2002). *Icarus*). In another paper, on the early temperature history of Earth, oxygen isotope data were used to establish that the average Archean surface temperature exceeded $50^{0}C$ (Knauth and Lowe (Submitted). *Bulletin of the Geological Society of America*).

A study of impact−generated wildfires, which comprise one of the most severe impact−related environmental perturbations was completed (Kring and Durda (In Press). *Journal of Geophysical Research*, Planets). A simple 2−D model for predicting the thermal evolution of impact−generated hydrothermal systems was created for craters having diameters in the range of 20 to 200 km. More complex 3−D simulations tracing the thermal evolution of these systems are in development in order to further refine the spatial and temporal distribution of habitable zones within impact−generated hydrothermal systems, based on the inferred temperature requirements for thermophilic and hyperthermophilic organisms. In addition, a model−based study of impact cratering in the inner Solar System revealed that a period of intense late bombardment is likely to have affected the Earth ~4 billion years ago. Models suggest that >20,000 impact craters with diameters ranging from 20 km to 5,000 km, would have been produced during a brief interval of activity. This would have resurfaced much of the planet (Kring and Cohen (2002). *Journal of Geophysical Research,* Planets). The period of intense late bombardment may have delayed the origin of life or affected its early evolution. This study also concludes that asteroids, and not comets, were the more likely impactors and that this late bombardment affected planets throughout the inner Solar System, including Mars.

Lower Cambrian Ecosystem Structure and Function

The sudden appearance of animal life at the base of the Cambrian marks a singular event in the history of our biosphere. In an incredibly short interval of geologic time (<10 million years), representatives of all of the modern skeletonized animal phyla appeared. With the addition of large herbivores and predators, a new global ecology emerged. The factors that triggered this important transition have been the subject of ongoing debate. Suggested mechanisms include such things as the buildup of photosynthetic oxygen to the threshold levels required for oxidative metabolism, biogeochemical factors leading to skeletonization, and the evolution of the genetic regulatory systems required for complex morphogenesis. The rise of large, multicelled bottom dwellers is also broadly correlated with the decline of stromatolites, the fossilized biosedimentary structures produced by microbial mats. The disappearance of stromatolites has been attributed to competitive exclusion by algae or disturbance by invertebrate grazers.

To better understand the ecological interactions that may have prevailed during the Cambrian transition, an interdisciplinary team of ASU and Mexican scientists has been studying the ecology of simple, microbiallybased (fish−snail−microbial mat) ecosystems of modern desert spring environments in the Cuatro Cienegas Basin, Central Mexico. Goals of the study include an improved understanding of the energy flow within simple ecosystems, of ecological factors contributing to explosive evolution within the highly endemic clades that inhabit the basin, of the nature of ecological interactions between grazers and stromatolite−producing microbial−mat communities, and of mechanisms of microbial fossilization. This unique interdisciplinary study aims to test specific hypotheses about the ecological mechanisms that may have contributed to the Cambrian explosion and the late Proterozoic decline of stromatolites, including novel ideas about stoichiometric constraints on evolution, arising from disparities in C:N:P (carbon, nitrogen, phosphorus) availability to grazers in such systems.

Ecological work during Year 4 characterized nutrient availability in habitats along the Churince and Rio Mezquites drainages of the Cuatro Cienegas Basin. Environmental sampling showed that PO_4 (phosphate) is in short supply (relative to inorganic N and other potential limiting nutrients). The analysis of algal/cyanobacterial mats showed extremely high C:P and N:P ratios, suggesting that microbial mats in this system comprise poor food quality for grazers. To further test this hypothesis, a 3−week, P−fertilization experiment of oncoid−producing microbial mats and unfertilized controls was undertaken. The treatment was successful in lowering the C:P ratio of microbial biomass in Rio Mezquites stromatolites. The decrease in microbial C:P was associated with a stimulation of snail P content and RNA:DNA ratio, suggesting that their growth in the natural system is indeed limited by stoichiometric food quality (low dietary P−content). Elser also published a book with Robert Sterner on *Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere* (2002). Princeton University Press).

An extensive morphometric study of species of *Mexipyrgus*, a common snail genus in the basin; was completed (Tang and Roopnarine (Submitted). *Astrobiology Journal*). Results indicated an extraordinary degree of morphometric differentiation in this taxon. DNA analyses are also being carried out to determine if the observed morphometric diversity is accompanied by genetic differentiation and if so, at what level.

A basin−wide population genetic survey of mitochondrial and nuclear DNA for two pupfish species, *Cyprinodon bifasciatus* and *C. atrorus* was also completed (Echelle et al (Submitted). *Evolution*). The work is designed to determine whether physiological differences between *C. bifasciatus* and *C. atrorus* correlate with nonenvironmental differences.

A unique calcite−producing colonial cyanobacteria discovered in Posa Escobedo, Cuatro Cienegas Basin was studied (Garcia−Pichel et al (2002). *Journal of Phycology*). Cyanobacterial community structure along longitudinal transects in Rio Mezquites was characterized by using molecular techniques (Denaturing Gradient Gel Electrophoresis (DGGE)) applied to oncoid stromatolites and a new procedure was developed for DNA extraction from carbonate−dominated samples (Wade and Garcia−Pichel (Submitted, 2002). *Geomicrobiology*). In collaboration with German colleagues, calcium microelectrode studies of oncoid−forming biofilms from the Rio Mezquites were carried out in order to better understand the role of microbial metabolism in calcification.

Analyses of field samples from several dozen localities around the Cuatro

Cienegas basin were successful in establishing >2,500 cultures of Eubacteria in the laboratory, as well as a variety of archaebacterial isolates. Preliminary genetic analyses using Restriction Fragment Length Polymorphism (RFLP) indicates that each of the >2,500 Eubacteria isolates is genetically distinct.

Exploring for Life in the Solar System

The active involvement of ASU astrobiologists in NASA missions to Mars and Europa provides ongoing opportunities for NAI−supported research and training in the exploration for life elsewhere in the Solar System. Work is under way on three instruments for use on either current or planned missions to Mars, including the Thermal Emission Spectrometer (TES) instrument onboard the Mars Global Surveyor (MGS) orbiter (Christensen et al (2001). *Journal of Geophysical Research*, Planets), the THEMIS instrument (onboard the Odyssey orbiter); and two mini−TES instruments (to be launched with the Mars Exploration Rover (MER) mission in 2003). Data from the MGS and Odyssey instruments have continued to provide basic mineralogical information needed to explore the past distribution of water on Mars, and orbital data from the Galileo spacecraft have been used to test the hypothesis of liquid water environments on Europa, Ganymede, and Callisto. Remote sensing analog studies have provided insights into the interpretation of infrared mineral spectra for evaporite basin settings in Death Valley and the Mono Basin, and hydrothermal environments in Yellowstone. Recent work has focused on selecting favorable landing sites for future surface missions to Mars for conducting *in situ* investigations into past or present biosignatures and for sample return. And modeling of eutectic brines as a potential mechanism for the production of the modern seeps observed at high Martian latitudes has made contributions to studies of Mars' habitability.

Involvement of ASU astrobiologists in various Mars Program mission planning efforts continues to strengthen the NAI's contribution to NASA's missions. Co−I Greeley is the former Chair of the Mars Exploration Payload Assessment Group (MEPAG), the primary community−based science strategy group for the Mars Program. Co−I Farmer is the current MEPAG Chair, Chair of the NAI Mars Focus Group and the interim Chair of MEPAG's Astrobiology Science Steering Group. He organized several joint videocon−based discussions with members of these two groups to address key programmatic issues in Mars exploration. Farmer is also a member of NASA's Space Sciences Advisory Group and in that capacity has worked to promote broader astrobiological representation on NASA advisory committees. Greeley and Farmer are also members of the Mars Exploration Review Team (MERT) and Mars Ad Hoc Science Team (MAST), external oversight committees for the Mars Exploration Program. Farmer represented the NASA Astrobiology Institute and Solar System Exploration Program in a congressional hearing last summer that focused on the search for extraterrestrial life. In 2002, Greeley and Farmer were selected to be participating scientists on the Mars Exploration Rover Mission which will be launched in 2003 and Co−I Leshin is PI for a Mars Scout mission proposal (SCIM) that was funded by the NASA Mars Exploration Program for pre−Phase A studies over the past year.

<u>Astrobiological Exploration of Mars</u>: Mars Global Surveyor Thermal Emission

Spectrometer (TES) data continue to provide new information about the role of aqueous processes in shaping the history of Mars. Although no large−scale carbonate deposits have yet been detected, spectral evidence was obtained for the presence of H_2O−bearing minerals within Martian dust. Based on spectral details of the dust, it appears that zeolites are a possible candidate for the aqueous mineral component. TES data are also being used to refine the candidate landing sites for the 2003 Mars Explorer Rover (MER) mission. The Sinus Meridiani hematite deposit, discovered last year with TES data (Christensen et al (2001). *Journal of Geophysical Research*−Planets) remains a top destination choice for one of two Mars Exploration Rovers to be launched in 2003. On Earth, such coarse−grained (specular) hematite deposits only form in the presence of large amounts of water. Newly acquired images from the Thermal Imaging System (THEMIS) on the Odyssey orbiter are also being used to characterize the candidate landing sites. Many geologic details of the hematite site have been revealed with stunning clarity using THEMIS data, helping to further refine the geologic context of the hematite deposit.

Detailed mineralogical ground truth for remotely sensed analog sites for Mars located in the Badwater Basin of Death Valley was developed; the study builds on previous spectral studies (completed last year). MASTER (mid−infrared spectral) data were used to identify the locations of mineralogically pure, end−member pixels (carbonate, sulfate and silicates) within the basin. To establish ground truth, end member pixels were located and sampled for a detailed laboratory analysis of mineralogy. Laboratory methods included x−ray diffraction, electron microprobe, electron microscopy, thin−section petrography and point counting, and laboratory and ground−based spectral analysis (using TES analog spectrometers). To aid spectroscopic identifications, a mid−IR spectral library was also developed for evaporate minerals and added to ASU's spectral database for use by the TES and THEMIS project teams presently mapping Mars. Results of this study were used to establish abundance thresholds (for natural mixtures in the Badwater Basin) necessary for the detection of discrete evaporite deposits (especially carbonates, sulfates, and silicates, including zeolites). Results further suggested that at the coarse spatial of the TES instrument (3 km/pixel), detection of carbonates and sulfates is unlikely. However, at the enhanced spatial resolution of THEMIS (100 m/pixel), both carbonates and sulfates should be easily detected, provided they are present at abundances exceeding ~15%.

<u>Europa</u>: A study of the “mitten" feature on Europa, which represents the extrusion of ice onto the surface from subsurface sources was completed (Figueredo et al (In Press, 2002). *Journal of Geophysical Research*−Planets). As such, the mitten structure is a high priority target for future exploration of Europa for past or present life. Pole−to−pole geological mapping of Europa was completed for strips representing the leading and the trailing hemispheres in order to determine potential latitudinal or hemispheric asymmetries in ice−fracture patterns. Studies of ice deformation in another region of Europa provided evidence for crustal foreshortening, important for understanding deformation processes in Europa's crust. These activities have helped to further characterize the nature and evolution of surface and near−surface environments on Europa needed to further assess the potential for habitable zones of subsurface liquid water.